

ROOM TEMPERATURE MINERALIZATION OF CHEMICAL WARFARE AGENTS USING HYDROGEN PEROXIDE – Pd/C

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The deep oxidation of toxic organics and chemical warfare (CW) agent simulants using Pd/C and dioxygen or hydrogen peroxide at 80–90°C was recently demonstrated by Sen et al.¹ This process offers a chemical means of destroying CW materials in a manner traditionally achievable only by incineration. Our investigations of the common simulant dimethyl methylphosphonate (DMMP) have shown mineralization to inorganic phosphate using H₂O₂–Pd/C at 90°C. Oxidative cleavage of DMMP to methylphosphonic acid is most effective at room temperature, apparently due to reduced H₂O₂ decomposition. Similarly, GD and VX also showed oxidative cleavage at room temperature, and formation of inorganic phosphate. For HD and its simulant thiodiglycol, mineralization is also evident at room temperature.

INTRODUCTION

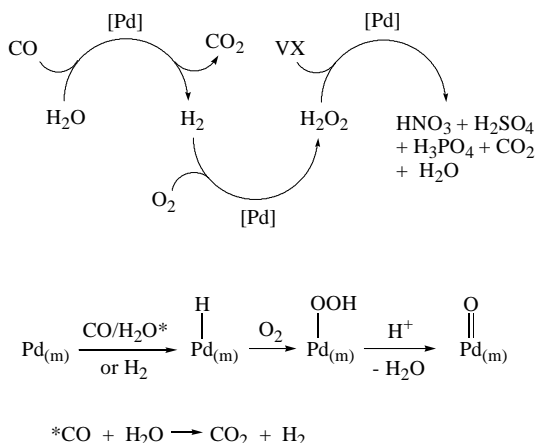
Historically, the demilitarization of chemical warfare agents has been accomplished by incineration, thus rendering the elements comprising the agents to their oxidized, mineral salts, i.e. CO₃²⁻, PO₄³⁻, SO₄²⁻, NO₃⁻, etc. However, concerns about the safety of incineration at storage sites, especially near populous areas, has prompted the adoption of chemical neutralization strategies.² Such methods require post-treatment of the non-toxic, neutralized products, e.g. by incineration or biodegradation, to yield mineral salts; the preferred state for ultimate disposal.²

Sen and coworkers¹ recently demonstrated the mineralization of organophosphorus and organosulfur compounds using Pd/C, O₂ and CO or H₂ at 80–90°C. The proposed mechanism, shown in Scheme 1 for VX, involves the following steps: 1) initially, H₂ (or H₂ formed in the water gas shift reaction* from CO) generates a metal-hydride; 2) the metal-hydride reacts with O₂ to yield a metal-hydroperoxide; and 3) the metal-hydroperoxide forms the active oxidant, a metal-oxo species. It is this latter species that is thought to carry out the observed deep oxidations of heteroatom organics. Thus in an aqueous setting, VX would yield nitric, sulfuric, phosphoric and carbonic acid (the latter evolving CO₂ under acidic conditions) as shown in Scheme 1. Alternatively, the metal-hydroperoxide, and subsequently the metal-oxo, may be generated directly from H₂O₂, and Sen et al.¹ proved that replacing the gases with aqueous H₂O₂ did yield similar deep oxidation behavior for phenol. As attractive as working with heated, pressurized O₂ and H₂ or CO may be, aqueous H₂O₂ is perhaps more acceptable for the demilitarization of CW agents. This is especially true if the reactions could be performed at room temperature. Indeed hydrogen peroxide-based decontaminants³ are gaining popularity among military

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and civil defense planners. The intent of the current study is to explore the mineralization of VX, GD and HD using the H_2O_2 –Pd/C system.

SCHEME 1



EXPERIMENTAL

50% H_2O_2 and 5% Pd/C (Degussa type E101) were obtained from Aldrich. Reactions were carried out in a stirred glass vessel by adding Pd/C, substrate, 50% H_2O_2 and, in some cases, water and conc. HCl. The H_2O_2 was either added all at once or metered in slowly with a syringe pump. Caution: the reaction of 50% H_2O_2 with 5% Pd/C is highly exothermic and results in substantial H_2O_2 decomposition! At selected intervals, ca. 1 mL aliquots were taken for NMR analysis. ^1H , ^{13}C and ^{31}P NMR spectra were obtained using a Varian Unityplus 300 NMR spectrometer. Chemical shifts were referenced to external TMS (^1H , 0 ppm), CDCl_3 (^{13}C , 77.0 ppm) and 85% H_3PO_4 (^{31}P , 0 ppm). A sample of the HD reaction was also analyzed by capillary electrophoresis (CE) using a Hewlett Packard ^{31}P CE system employing indirect UV detection to confirm SO_4^{2-} formation, i.e. mineralization.

RESULTS AND DISCUSSION

Data obtained for various simulants and agents are given in Table 1. Initial studies were carried out with DMMP with the intention of detecting inorganic phosphate (PO_4^{3-}) by ^{31}P NMR, thus proving oxidative cleavage of the P-C bond and mineralization of the phosphorus. However, this conclusive proof was hampered by two phosphorus-containing stabilizers present in the 50% H_2O_2 ; one of which was PO_4^{3-} itself. For the DMMP reactions reported in Table 1, no substantial PO_4^{3-} formation was evident, and the conversions reported in Table 1 merely reflect the amount of DMMP remaining compared to detected products. These products varied with temperature. At 90°C, both methyl methylphosphonic acid (MMPA) and methylphosphonic acid (MPA) formed, but at room temperature, decomposition occurred directly to MPA. A possible explanation for this difference is that the reaction pathway $\text{DMMP} \rightarrow \text{MMPA} \rightarrow \text{MPA}$ is expected for simple hydrolysis, which would be competitive with oxidative cleavage at elevated temperatures. At room temperature, the lone MPA product is consistent with exclusive oxidative cleavage. The overall conversions at 90, 50°C and room temperature were 94.2, 35 and 100%, with the latter conversion achieved using only 5.63 mL H_2O_2 (compared to 10 mL for the other reactions). At 50°C no MMPA hydrolysis product was observed, and oxidative cleavage was the major mechanism. The low conversion is attributed to heightened H_2O_2 decomposition at elevated temperatures. The high conversion at 90°C is largely attributed to hydrolytic cleavage. Thus oxidative cleavage appears most effective at room temperature, where undesired H_2O_2 decomposition is minimized. For the reactions

shown in Table 1 no substantial PO_4^{3-} formation beyond that of the H_2O_2 background was observed; a testament to the resiliency of the P-C bond. Yet, as anticipated, in extended reactions done with DMMP at 90°C , and for GD and VX at *room temperature* (see below), significant additional PO_4^{3-} was detected after several days.

TABLE 1.

Substrate	Temp	Pd/C ^a	H ₂ O	HCl ^b	H ₂ O ₂ ^c	Time	Conversion ^d
25 μL DMMP ^e	90°C	250 mg	5.63 ml	1.87 ml	10 ml	20 h	94.2%
25 μL DMMP	50	250	5.63	1.87	10	22	35.0
25 μL DMMP	22	250	none	1.87	5.63	24	100
23 μL TG ^f	22	250	none	none	5	72	>91 ^g
38 μL HD	22	250	none	none	10	24	100 ^h
81 μL VX	22	250	none	none	10	24	96.3
55 μL GD	22	250	none	none	10	24	79.6
					10 ⁱ	24	100

^a5 wt% Pd. ^bConc. HCl. ^c50% H_2O_2 . ^d $[1 - (\text{moles substrate}/\text{moles product})] \times 100$. ^eDimethyl methylphosphonate. ^fThiodiglycol. ^gLower limit estimate; product interfered with TG detection. ^hHD completely hydrolyzes to TG in water. ⁱSecond H_2O_2 addition allowed to react for an additional 24 h.

For TG and HD reactions at *room temperature*, ^1H NMR showed definite loss of C-H bond intensity relative to a TG control sample (Figure 1). Furthermore, the all important sign of mineralization, SO_4^{2-} , was observed by capillary electrophoresis. However, HCO_3^- was not observed,

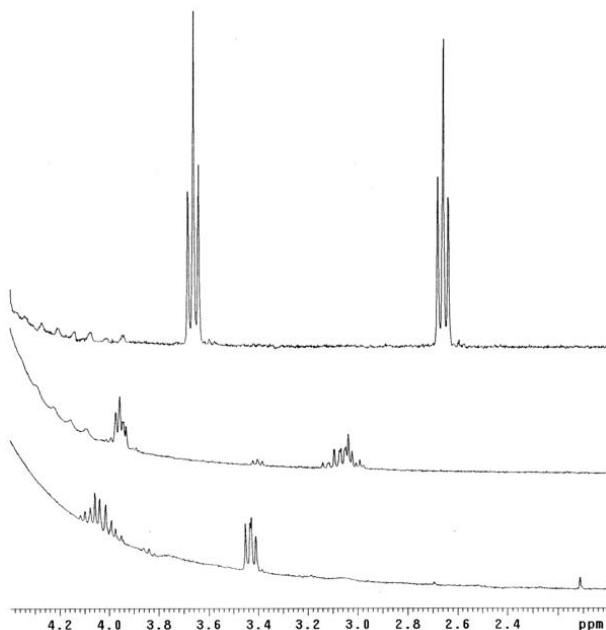
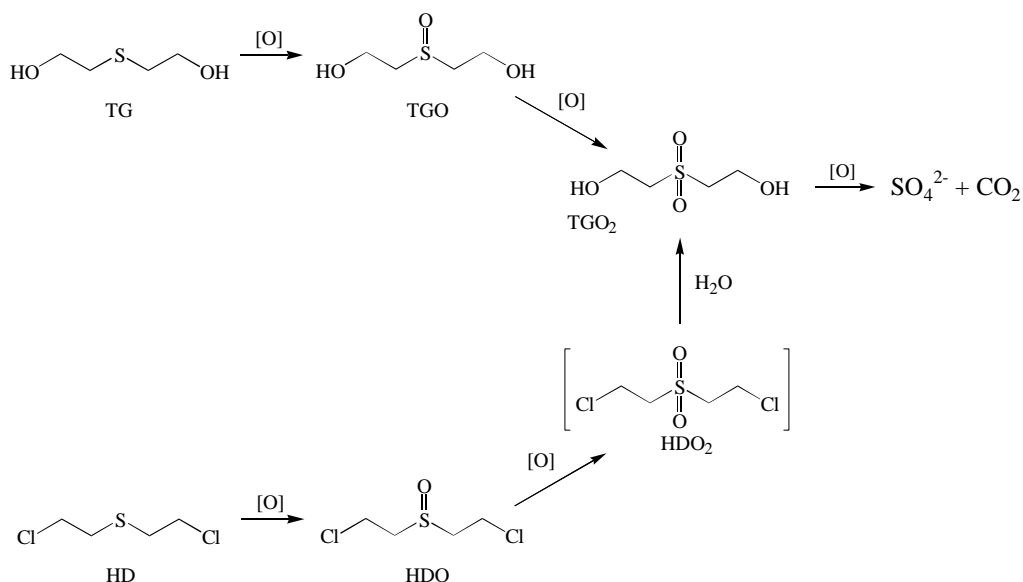


Figure 1. ^1H NMR spectra obtained for TG control (top) and TG (middle) and HD (bottom) reaction mixtures (see Discussion).

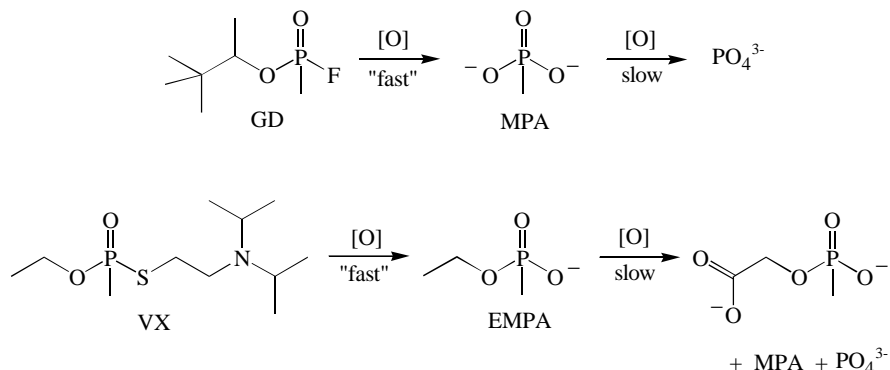
consistent with the evolution of CO_2 as shown in Scheme 2. ^1H NMR showed that TG reacted to the sulfoxide (TGO) and sulfone (TGO₂), but no further products were observed. As detected by ^1H NMR and confirmed by ^{13}C NMR, the initial HD product was the sulfoxide (HDO, ^{13}C : 53.7, 37.3 ppm), which proceeded directly to TGO₂ (^{13}C : 55.0, 54.4 ppm) (Scheme 2). No other products were observed. Thus intermediates involved in the passage of TGO₂ into mineral oblivion must be short lived. For HD, the non-detection of HD-sulfone (HDO₂) or TGO is consistent with the facile hydrolysis of HDO₂ to TGO₂ and the extreme hydrolytic stability of HDO.⁴

SCHEME 2



Similar to DMMP, the detected products for GD (MPA) and VX (EMPA) indicate *room temperature* oxidative cleavage of their pinacolyl and 2-(diisopropylamino)ethanethiol groups, respectively (Scheme 3). As shown by the conversions in Table 1, these reactions require a day or two to complete, with the VX reaction occurring somewhat faster. Over the course of several days, substantial increases in the amounts of PO_4^{3-} are observed in these reactions. For GD, this increase corresponded to the decrease in the amount of MPA (Scheme 3). The reaction was more complex for VX, where the initially formed EMPA degraded to MPA, PO_4^{3-} and an unknown phosphonate postulated as acetyl methylphosphonic acid. This tentative assignment is made based on a similar product, phosphonoacetic acid, observed by Sen et al.¹ in the oxidation of triethylphosphine oxide.

SCHEME 3



CONCLUSIONS

GD, VX and HD are mineralized at room temperature using the Pd/C-catalyzed peroxide system. Mineralization of HD and the oxidative cleavage of the pinacolyl and 2-(diisopropylamino)ethanethiol groups of GD and VX are facile compared to the slow oxidative cleavage of the P-C bond of MPA.

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